Supporting Information

Mixed Matrix PVDF Membranes With In Situ Synthesized PAMAM Dendrimer-Like Particles: A New Class of Sorbents for Cu(II) Recovery from Aqueous Solutions by Ultrafiltration

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EXPERIMENTAL METHODS AND PROCEDURES

Chemicals and Materials

Polyvinylidene fluoride (PVDF) [Kynar 761] was provided by Arkema (King of Prussia, PA, USA). G0-NH_2 and G1-NH_2 PAMAM dendrimers were purchased as methanol solutions (~34 wt%) from Dendritech Inc, USA. Table S1 lists selected physical-chemical properties of the PAMAM dendrimers. Epichlorohydrin (ECH) was purchased from Sigma-Aldrich. Triethyl phosphate (TEP), ethanol and nitric acid (60 wt% HNO_3) were purchased from Daejung Chemicals (South Korea). Hydrochloric acid (12 M HCl) was purchased from Junsei (South Korea). Sodium hydroxide (NaOH pellets) and copper(II) nitrate trihydrate (ACS purus grade) were purchased from Sigma-Aldrich. A standard solution of copper (Cu) [10 mg/L in 5wt% HNO_3] (Multi-element calibration standard-2A) was purchased from Agilent Technologies. All chemicals were used as received. All aqueous solutions were prepared using Milli-Q deionized water (DIW) with a resistivity of 18.2MΩcm and total organic content < 5 ppb.

Membrane Preparation

The membrane preparation procedures were adapted from our previous work [1]. The membranes were prepared using a combined thermally-induced phase separation (TIPS) and non-solvent induced phase separation (NIPS) process. Table S2 lists the compositions of the membrane casting solutions. A control PVDF membrane and two mixed matrix PVDF membranes with *in situ* synthesized PAMAM particles (MDP-G0 and MDP-G1) were prepared using the three-step process given below. The recipe used to prepare the mixed matrix membranes (MMMs) was selected to achieve a high particle loading (~50 wt%) based on the results of our previous work on mixed matrix PVDF membranes with *in situ* synthesized PEI particles [1]. The MDP-G0 and MDP-G1 membranes were prepared using G0-NH_2 and G1-NH_2 PAMAM dendrimers as particle precursors, respectively.

1) Preparation of Membrane Casting Solutions. A typical membrane casting solution was prepared by mixing the required amounts of PVDF and TEP in a three neck round-bottom flask equipped with a condenser and an overhead stirrer. A homogeneous PVDF dope solution was obtained after mixing for 24 hours at 80 °C. Following this, the prepared PVDF dope solution was transferred into a glass container and covered with aluminum foil.

2) In Situ Synthesis of Crosslinked PAMAM Dendrimer Particles. Prior to membrane casting, the PVDF dope solution was homogenized at 4000 rpm for 7 minutes using a Silverson L5M high shear mixer (HSM). During the homogenization, the temperature of the dope solution was raised to 80 °C and kept constant. A solution of PAMAM in TEP was then added drop wise to the PVDF dope solution for 5 minutes followed by high shear mixing for 15 minutes to obtain a homogeneous PVD+PAMAM dispersion in TEP. A solution of ECH in TEP was then added drop wise to the dispersion and homogenized for 5 minutes under similar HSM conditions to obtain a stable dispersion of PAMAM particles in the PVDF+TEP dope. Finally, the curing reaction was continued in a round bottom flask equipped with an overhead stirrer at 80 °C for 3 hours.

3) Membrane Casting. Following the completion of the curing reactions, the dispersion of PVDF+TEP+ECH crosslinked PAMAM particles dope was allowed to cool to ambient temperature to initiate the TIPS step of the membrane casting process. The membranes were prepared with and without a polyethylene terephthalate (PET) microporous support. To prepare a membrane without support, the cooled dispersion of PVDF+PAMAM particle in TEP was poured onto a clean glass plate. A casting knife (BYK Chemie) [with 300 μm air gap] was used to uniformly coat the casting solution onto the glass plate. The nascent membrane was kept for 30 seconds at ambient temperature (25 ± 1°C, RH: 55%) followed by immersion into a DIW bath with a temperature of 23 ± 1°C. After 1 hr, the nascent membrane was transferred to a fresh DIW bath and immersed for 24 h. Following this, the membrane was soaked in ethanol for 10 h. Finally, the membranes were air dried and stored in a desiccator. A similar procedure was used to prepare a membrane with microporous support by pouring the casting solution on a PET non-woven fabric. The supported membranes were stored in DIW with the water periodically replaced with fresh DIW until the metal binding experiments were initiated.

Membrane Characterization

1) Membrane Morphology. The cross-sectional and top surface of each membrane was imaged with a field emission scanning electron microscope (FESEM, Magellan Series 400, FEI Corporation) at an acceleration voltage of 2.0 kV. Before imaging, all samples were first coated with platinum for 30 seconds followed by osmium for 30 seconds to minimize the charging effect. To obtain the membrane cross section morphology, the membranes were frozen and fractured following immersion in liquid nitrogen. The SEM images were subsequently analyzed to estimate membrane thickness and PAMAM particle size using the Image J Version 1.45m image processing/analysis software [2].

2) N_2 Adsorption Permporometry. The average pore diameter of each membrane top/skin layer was determined by N_2 adsorption permporometry [3] at 77 K using a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer. The Barrett-Joyner-Halenda (BJH) methodology was utilized to extract membrane pore diameters from the N_2 adsorption/desorption data [4].

3) Membrane Surface Composition. The surface chemical composition was characterized by Fourier transform infrared (FT-IR) spectroscopy. The mid IR spectra (500 cm^{-1} to 4000 cm^{-1}) of the membranes were scanned in attenuated total reflectance (ATR) mode. The spectra were acquired by averaging 32 scans at a resolution of 2 cm^{-1} using a JASCO 4100 FT-IR spectrometer (Japan) and a zinc selenide ATR crystal plate with an aperture angle of 45°. In contrast, the near IR (NIR) spectrum of each membrane (4000 cm^{-1} to 10000 cm^{-1}) was recorded by reflection using a Bruker MPA FT-NIR spectrometer equipped with a quartz beam splitter and an external RT-PbS detector. The NIR spectra were acquired by averaging 32 scans at a resolution of 8 cm^{-1}. The elemental composition of each membrane surface was analyzed by X-ray photoelectron spectroscopy (XPS) using an SSX-100 UHV spectrometer from Surface Science Instruments. The sample was irradiated with a beam of monochromatic Al Kα X-rays with energy of 1.486 keV.

4) Contact Angle Measurements. The hydrophobicity of each membrane was determined from contact angle measurements using a Phoenix 300 contact angle analyzer. A micro syringe was utilized to place a water droplet on the surface of each membrane. After 30 and 120 seconds, the image was captured and analyzed using the instrument's image processing software. Each reported contact angle is the average of five different measurements.

5) Particle Size Measurements by DLS. A 0.2 g of dry membrane was added to 20 g of TEP solvent in sample vial. It was allowed for dissolution for 15 hours at ambient temperature as a result fine dispersion was obtained. Then the dispersion was sonicated for 15 minutes. A 1.0 mL aliquot was sampled from the dispersion and diluted with 10mL of TEP solution for the DLS measurements. These were conducted in duplicate at 25 °C using TEP solvent.

6) Zeta Potential Measurements. The zeta potentials of the membranes were determined using the electrophoresis method [5]. An ELSZ-2 electrophoretic light scattering spectrophotometer from Otsuka Electronics, Japan [with a plate quartz cell as membrane holder] was employed to measure the electrophoretic mobility of the monitoring particles. The monitoring particles consisted of polystyrene (PS) latex particles (Otsuka Electronics, Japan) with an amide surface coating and

diameter of 520 nm. The PS particles were dispersed in 0.01 M NaCl solutions at pH 7.0. The measured electrophoretic mobilities (U) of the monitoring PS particles [$cm^2/(V.s)$] were utilized to calculate membrane zeta potentials (ς) [mV] using the Smoluchowski equation as given below [5]:

$$\varsigma = \frac{4\pi\eta U}{\varepsilon_r \varepsilon_0} \qquad \text{Eq 1}$$

where η is the liquid viscosity (0.89×10^{-3} Pa.s), e_r is the relative permittivity of liquid (78.38) and e_0 is the vacuum permittivity (8.854×10^{-12} $s.m^{-1}$).

Copper Filtration and Binding Studies

The Cu(II) filtration and binding experiments were conducted on a custom-made cross-flow UF system with an active filtration area of 24 cm^2. The filtration cell (17.62 cm in length; 2.54 cm in width and 0.3 cm in depth), pump head, reservoir and tubing were built using Teflon and polyvinyl chloride (SI Figure S1) to eliminate metal ion sorption onto the system components. The flow rate was maintained at ~ 1.7 L / min with a crossflow velocity of ~37.2 cm/s. Each filtration experiment consisted of four steps. The pH of the feed water was adjusted with a solution of 0.1 N HCl or 0.1 N NaOH as needed. Each membrane was first compacted by running DIW for 1 hour at a pressure of 3 bar. The pressure was then reduced to 2 bar and aliquots of permeate were collected every 5 minutes for 1 hour to estimate membrane water flux. Following this, a constant-pH solution was pumped through each membrane and aliquots of permeate were collected every 5 minutes for 30 minutes. After the completion of the constant-pH water flux measurements, a 2 L of a solution of Cu(II) [10 mg/L] at constant pH (3, 7 and 9) was pumped trough each membrane at 2 bar. In this case, permeate samples were collected every 5 minutes for 3 hours. Following the flux measurements, the permeate samples were poured back into the UF system feed tank (SI Figure S1) to keep the volume of the feed (2 L) constant; i.e. within 2%. The permeate flux (J_n) [L m^{-2} hr^{-1}] at time t_n through each membrane was expressed as:

$$J_n = \frac{V_P}{A t_n} \qquad \text{Eq. 2}$$

where V_p is the volume of permeate (L) collected at time t_n (hr) and A is the effective membrane area (m^2). For the Cu(II) binding assays, aliquots (1 mL) of feed and permeate solutions were sampled every 5 minutes for a period of 1 hour and then every 30 minutes for the remainder of the run time. The collected samples were diluted with a 3wt% HNO_3 solution and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent ICP-MS 7700x

instrument. The mass of Cu(II) bound $M^{m}_{t_n}$ (mg per mL of dry membrane) at time t_n was expressed as:

$$M^{m}_{tn} = \frac{(V^{F}_{t_n} C^{F}_{t_n} - V^{P}_{t_n} C^{P}_{tn})}{A_m d_m} \qquad \text{Eq.3}$$

where V^{F}_{tn} and V^{P}_{tn} are, respectively, the volumes of feed and permeate at time t_n; C^{F}_{tn} and C^{P}_{tn} are, respectively, the copper concentrations in the feed and permeate at time t_n, and A_m and d_m are, respectively, the membrane area and thickness. To account for the addition of a permeate sample in the feed following the completion of a flux measurement, a corrected copper correction in the feed at time t_n ($n > 0$) was estimated by mass balance using the equation given below:

$$C^{F}_{t_n} = \frac{C^{F}_{t_{n-1}} V^{F}_{t_{n-1}} + C^{P}_{tt_{n-1}} V^{PSF}_{t_{n-1}}}{V^{F}_{t_{n-1}} + V^{PSF}_{t_{n-1}1}} \qquad \text{Eq.4}$$

where $C^{F}_{t_n}$ and $C^{F}_{t_{n-1}}$ are, respectively, the copper concentration in the feed at times t_n and t_{n-1}; $C^{P}_{t_{n-1}}$ is copper concentration in the permeate at time t_{n-1}; $V^{F}_{t_{n-1}}$ is the volume of feed at time t_{n-1} and $V^{PSF}_{t_{n-1}}$ is the volume of permeate sample that was poured back to the feed at time t_{n-}.

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Table S1. Selected physicochemical properties of the PAMAM dendrimers that were utilized as particle precursors for the mixed matrix PVDF membranes with *in situ* synthesized PAMAM particles. The data were taken from Dendritech (http://www.dendritech.com/pamam.html).

Dendrimer	[a]M_{wth} (Dalton)	[b]N_{Pamine}	[c]N_{Tamine}	[d]N_{Amide}	[e]C_{Pamine} (meq/g)	[f]C_{Tamine} (meq/g)	[g]C_{Amide} (meq/g)	[h]C_{Ligand} (meq/g)	[i]D_H (nm)
G0-NH_2	517	4	2	4	5.56	2.78	5.56	19.47	1.5
G1-NH_2	1430	8	6	12	4.00	3.00	6.00	18.99	2.2

[a]Mwth: theoretical molecular weight.
[b]N_{Pamine}: number of primary groups.
[c]N_{Tamine}: number of tertiary amine groups.
[d]N_{Amide}: number of amide groups. Each amide group has 2 potential electron donors: 1 N donor and 1 O donor.
[e]C_{Pamine} and [f]C_{Tamine} are, respectively, the concentrations of primary and tertiary amino groups per gram of PAMAM respectively.
[g]C_{Amide} and [h]C_{Ligand} are the concentration of amide and ligand functionalities per gram of PAMAM respectively.
[i]D_H: theoretical hydrodynamic diameter of dendrimer molecule.

Table S2. Compositions of the casting solutions, neat PVDF membrane and mixed matrix PVDF membranes with *in situ* synthesized crosslinked PAMAM particles that were prepared in this study.

Membrane	MDP-G0		MDP-G1		PVDF (Neat)	
	M (g)	wt (%)	M (g)	wt (%)	M (g)	wt (%)
A. Compositions of Membrane Casting Solutions						
[a)]PVDF	18.0	11.00	18.0	10.99	18.0	15.0
[b)]PAMAM + [c)]ECH	19.46	11.90	19.46	11.88	--	--
[d)]TEP	120.1	73.46	120.1	73.31	102.0	85.0
[e)]PAMAM Solution (Methanol)	5.95	3.64	6.27	3.83	--	--
B. Estimated Membrane Compositions (Dry mass wt%)						
PVDF	18.0	52.29	18.0	52.29	18.0	100
[1]Crosslinked PAMAM particles	16.43	47.71	16.43	47.71	--	--
C. Estimated degree of crosslinking of PAMAM particles based on ECH concentration (Dry mass wt%)						
[2]ECH	7.71	39.62	7.71	39.62	--	--
PAMAM	11.75	60.38	11.75	60.38	--	--

[a)] PVDF: Polyvinylidene fluoride; [b)] PAMAM: Polyamidoamine; [c)] ECH: Epichlorohydrin;
[d)] TEP: Triethyl phosphate; [e)] Methanol solutions of G0-NH_2 PAMAM (33.6 wt%) and G1-NH_2 PAMAM (34.79 wt%).

[1]The mass fraction of crosslinked PAMAM particles in each membrane was estimated based on the following assumptions:
i) All ECH crosslinker molecules were reacted with the segregated PAMAM molecules by the reaction between epoxy & chloro groups of ECH and primary/secondary amino groups of PAMAM molecules in the dope solutions (Figure 1B).
ii) Each ECH molecule produces one molecule of hydrogen chloride (HCl) following the crosslinking reaction (Figure 1B).
iii) All unreacted PAMAM molecules were washed away in the coagulation bath and subsequent membrane washes with methanol and DIW.

[2]The weight fraction (dry mass wt%) of ECH was taken as a surrogate for the degree of crosslinking of the PEI based on our previous work on the synthesis of perchlorate-selective resin beads [6].

Table S3. Estimated diameters of the embedded PAMAM particle of the mixed matrix MDP-G0 and MDP-G1 membranes using FESEM with the image processing/analysis software ImageJ.[1]

Image No	Particle Diameter (nm)	
	MDP-G0	MDP-G1
1	1867	2572
2	2370	3127
3	383	2459
4	1293	3342
5	1029	2411
6	814	3055
7	335	1361
8	359	740
9	2968	2817
10	1269	2530
Average Diameter (nm)	1269	2441
Minimum (nm)	335	740
Maximum (nm)	2968	3342

Table S4. Permeate fluxes of aqueous solutions Cu(II) [10 mg/L] trough the mixed matrix MDP-G0 and MDP-G1 membranes as a function of filtration time at 2 bar pressure

Time (Minutes)	Flux (LMH)					
	MDP-G0			MDP-G1		
	pH 3.0	pH 7.0	pH 9.0	pH 3.0	pH 7.0	pH 9.0
0	--	--	--	--	--	--
5	342.31	345.6	529.12	96.15	78.57	36.81
10	336.81	348.35	499.45	90.11	70.33	36.81
15	329.67	324.18	485.16	86.26	67.58	37.91
20	321.43	324.73	471.43	84.62	64.84	38.46
25	312.64	307.69	466.48	82.42	65.38	37.36
30	304.95	319.23	445.6	80.77	63.19	40.66
35	298.9	336.26	440.66	79.12	61.54	36.26
40	295.05	320.88	428.57	76.92	59.89	36.26
45	287.91	339.01	425.82	76.92	61.54	35.16
50	281.32	327.47	418.13	77.47	61.54	38.46
55	278.57	307.69	415.38	76.37	59.89	35.71
60	274.73	293.41	415.38	75.27	59.34	36.26
90	250.55	258.24	386.26	72.25	58.97	38.55
120	233.52	270.88	392.86	68.13	57.42	41.48
150	221.98	278.02	373.63	63.19	58.15	42.95
180	213.19	275.82	395.05	58.97	58.42	42.58
Average	**286.47**	**311.09**	**436.81**	**77.81**	**62.91**	**38.23**
SD	**39.87**	**28.12**	**43.69**	**9.45**	**5.52**	**2.45**

Table S5. Extent of binding [mg of Cu(II) per mL of membrane] and mean % Cu bound in aqueous solutions by the mixed matrix MDP-G0 and MDP-G1 membranes as a function of filtration time and solution pH

Time (Mins)	pH 3.0				pH 7.0				pH 9.0			
	MDP-G0		MDP-G1		MDP-G0		MDP-G1		MDP-G0		MDP-G1	
	Cu(II) binding (mg/mL)	Cu bound (%)	Cu(II) binding (mg/mL)	Cu bound (%)	Cu(II) binding (mg/mL)	Cu bound (%)	Cu(II) binding (mg/mL)	Cu bound (%)	Cu(II) binding (mg/mL)	Cu bound (%)	Cu(II) binding (mg/mL)	Cu bound (%)
0	0	0	0	0	0	0	0	0	0	0	0	0
5	56.19	24.4	62.41	69.77	55.44	52.86	59.51	95.18	52.81	58.31	55.03	99
10	55.53	15.27	61.89	64.38	54.05	31.17	58.98	91.09	50.71	31.44	54.74	98.87
15	55.13	14.53	61.41	68.81	53.41	28.24	58.46	88.61	49.81	26.93	54.39	98.91
20	54.76	16.98	60.85	71.22	52.7	24.36	57.9	86.88	49.03	23.71	53.99	98.92
25	54.21	13.45	60.23	72.78	52.11	22.39	57.31	85.05	48.3	22.44	53.54	98.96
30	53.77	17.07	59.55	74.32	51.45	22.89	56.68	84.86	47.62	20.89	53.04	99.01
35	53.16	15.49	58.82	75.39	50.67	20.66	56.01	83.93	46.9	19.56	52.47	99.07
40	52.56	16.92	58.05	76.76	49.99	18.43	55.3	82.72	46.2	18.11	51.88	99.04
45	51.91	18.36	57.22	77.06	49.21	18.01	54.56	82.06	45.45	16.6	51.25	99.01
50	51.13	14.38	56.35	77.71	48.5	17.61	53.76	80.84	44.73	16.17	50.58	98.97
55	50.5	21.14	55.43	77.95	47.78	15.81	52.93	79.67	43.98	14.16	49.85	98.95
60	49.59	15.45	54.47	78.27	47.05	14.3	52.07	79.72	43.23	13.35	49.09	98.94
90	48.94	22.24	53.1	78.46	46.46	18.4	50.84	76.8	42.57	12.7	48.29	98.94
120	48.14	27.34	50.84	79.47	45.59	19.59	48.92	75.4	41.74	9.58	46.64	98.91
150	47.21	29.38	48.69	79.46	44.65	17	47.05	73.52	40.93	0.72	44.93	98.89
180	46.25	31.88	46.67	79.63	43.77	16.75	45.24	72.32	40.27	5.12	43.21	98.68
Average	**51.81**	**19.64**	**56.62**	**75.09**	**49.55**	**22.40**	**54.10**	**82.42**	**45.89**	**19.36**	**50.81**	**98.94**
SD	**3.12**	**5.80**	**4.79**	**4.51**	**3.51**	**9.30**	**4.32**	**6.28**	**3.68**	**12.97**	**3.58**	**0.09**

Figure S1. Picture of the crossflow ultrafiltration (UF) system used in the water filtration and Cu(II) binding measurements. The filtration cell (l7.62 cm in length; 2.54 cm in width and 0.3 cm in depth), pump head, reservoir and tubing were built using Teflon and polyvinyl chloride to eliminate metal ion sorption onto the system components.

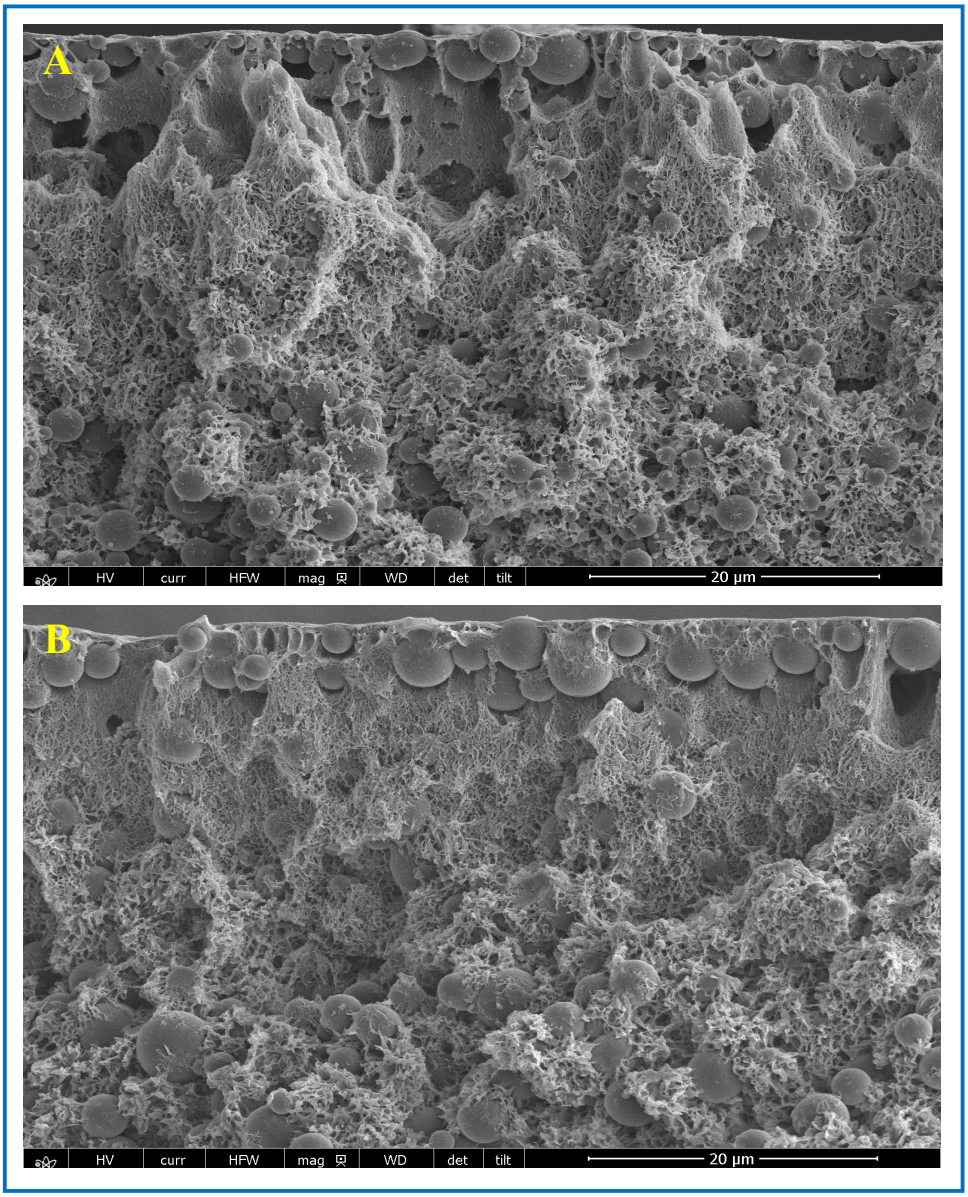


Figure S2. Magnified FESEM micrographs (1000 X) showing the presence of PAMAM particles at both the surface layers and inside the matrices of the mixed matrix PVDF membranes. Panel A: mixed matrix PVDF MDP-G0; Panel B: mixed matrix PVDF MDP-G1. The estimated composition of each membrane is listed in Table S2.

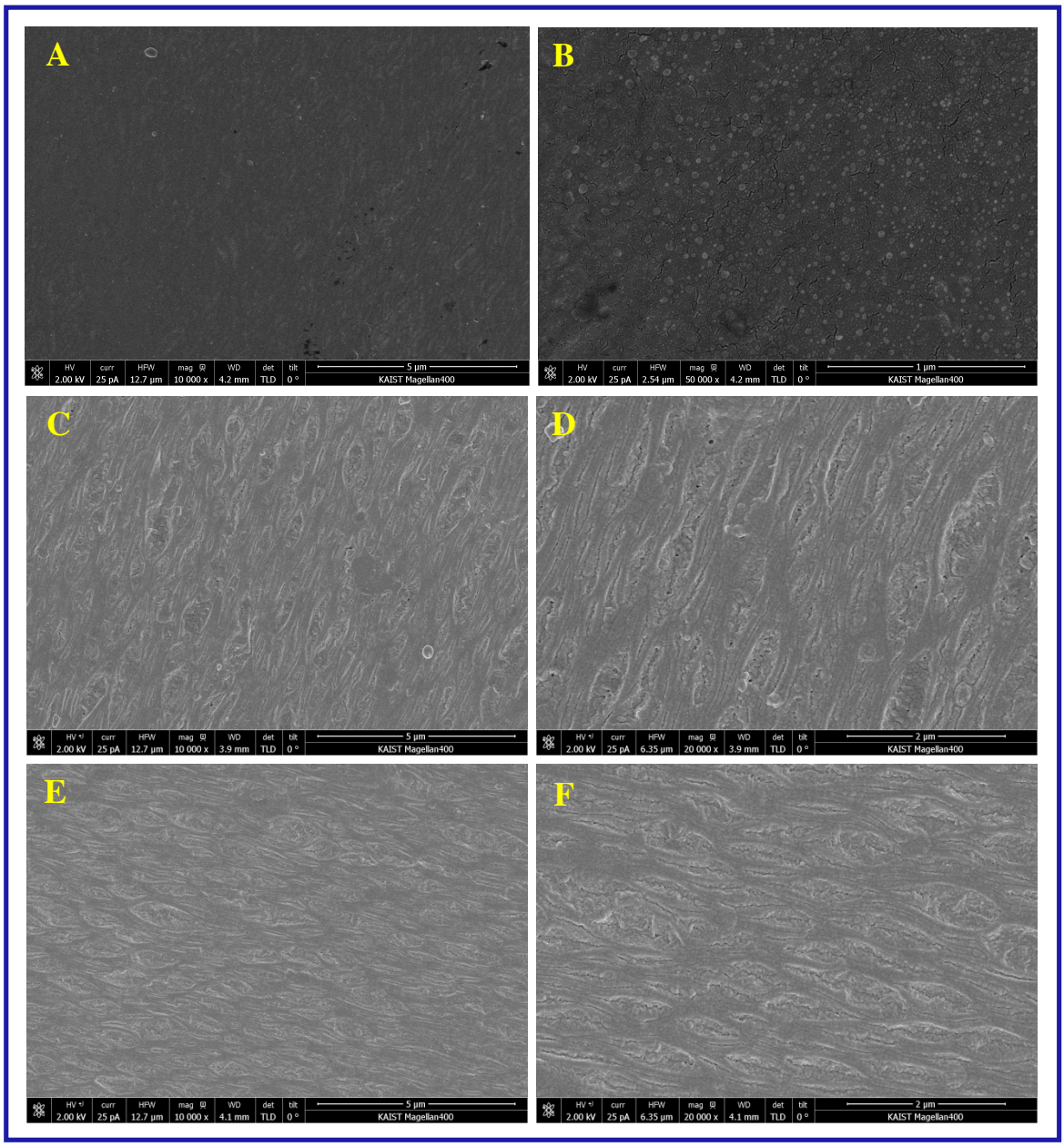
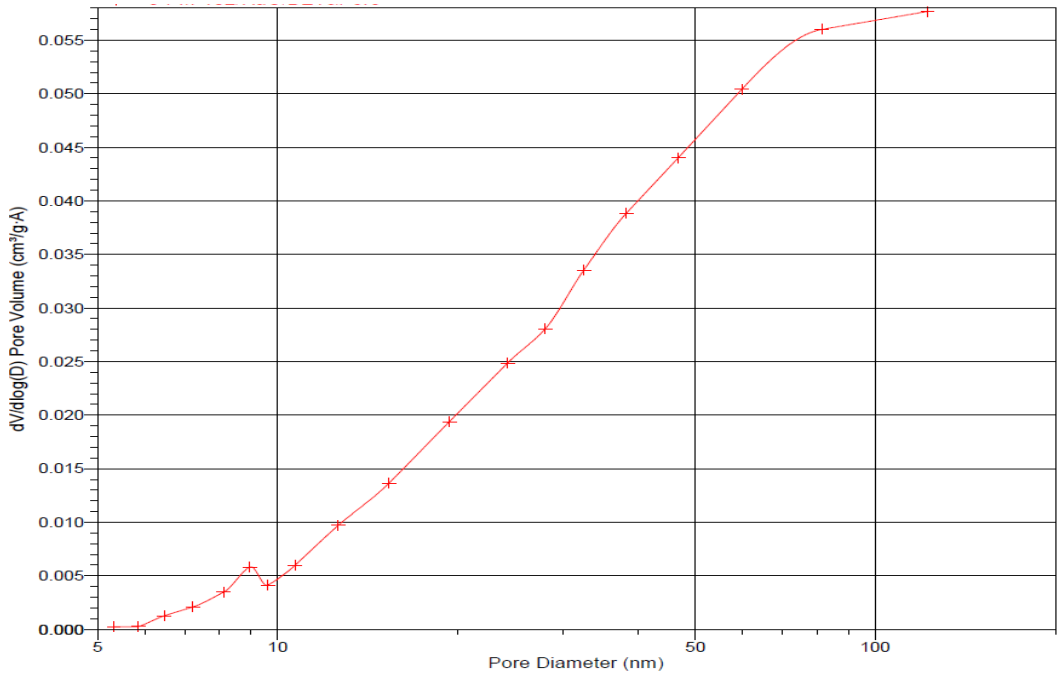


Figure S3. FESEM surface micrographs showing the top surfaces of mixed matrix PVDF membranes with *in situ* synthesized PAMAM particles. Panels A and B: pristine PVDF control membrane; Panels C and D: mixed matrix PVDF MDP-G0 membrane; Panels E and F: mixed matrix PVDF MDP-G1 membrane. The estimated composition of each membrane is listed in Table S2.

A. Barrett-Joyner-Halenda adsorption pore volume



B. Barrett-Joyner-Halenda desorption pore volume

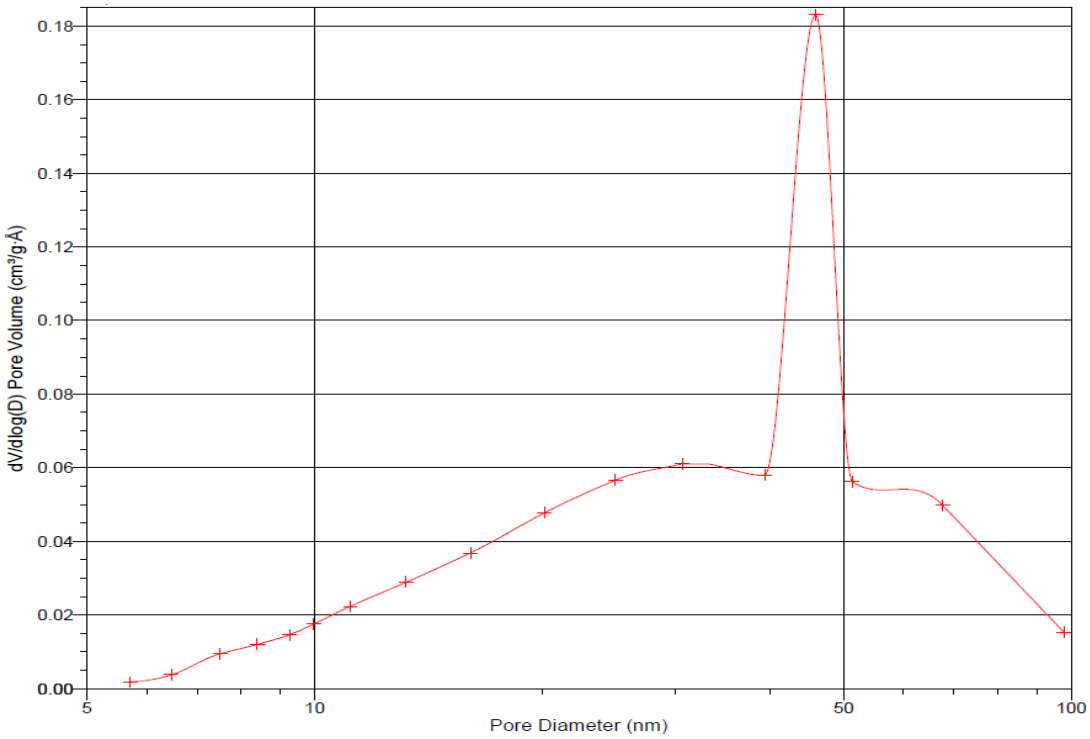
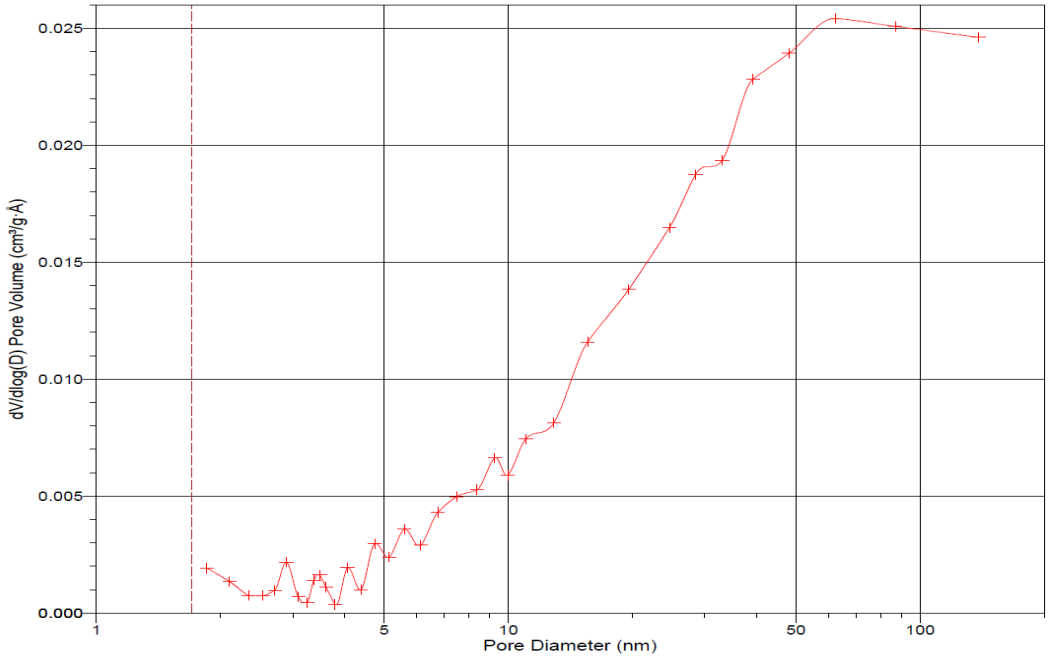


Figure S4. Characterization of the mixed matrix MDP-G0 membrane by N_2 adsorption permporometry. The pore diameters were estimated using the Barrett-Joyner-Halenda (BJH) methodology (4).

A. Barrett-Joyner-Halenda adsorption pore volume



B. Barrett-Joyner-Halenda desorption pore volume

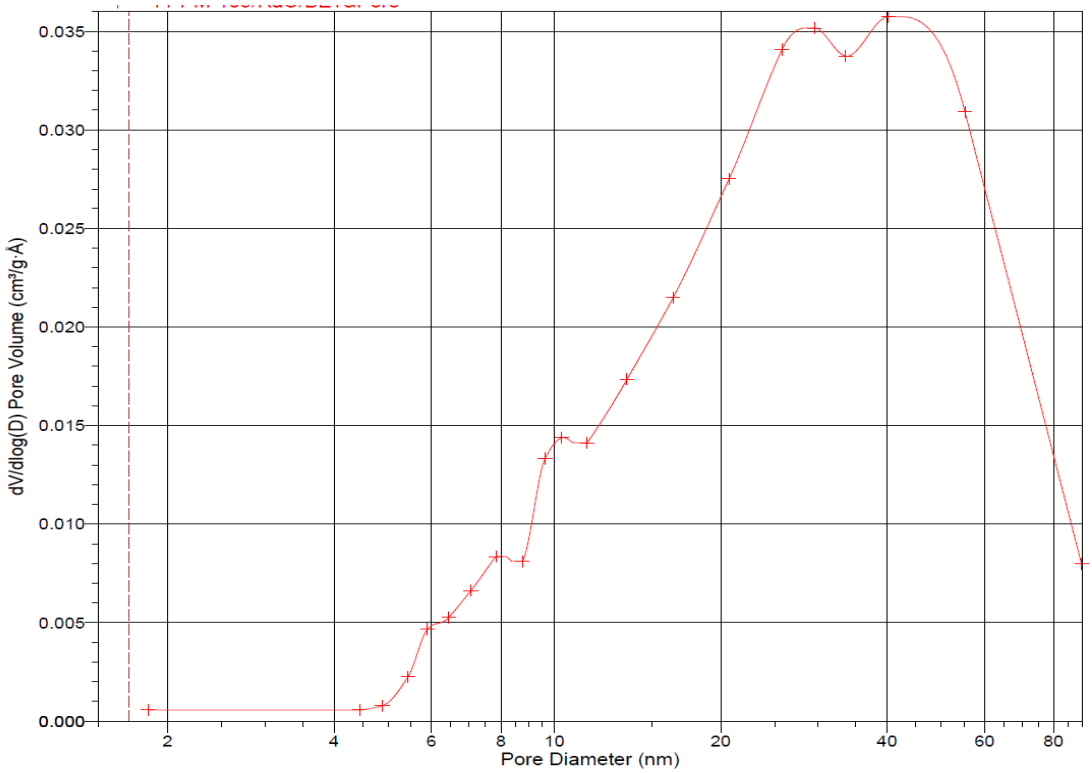
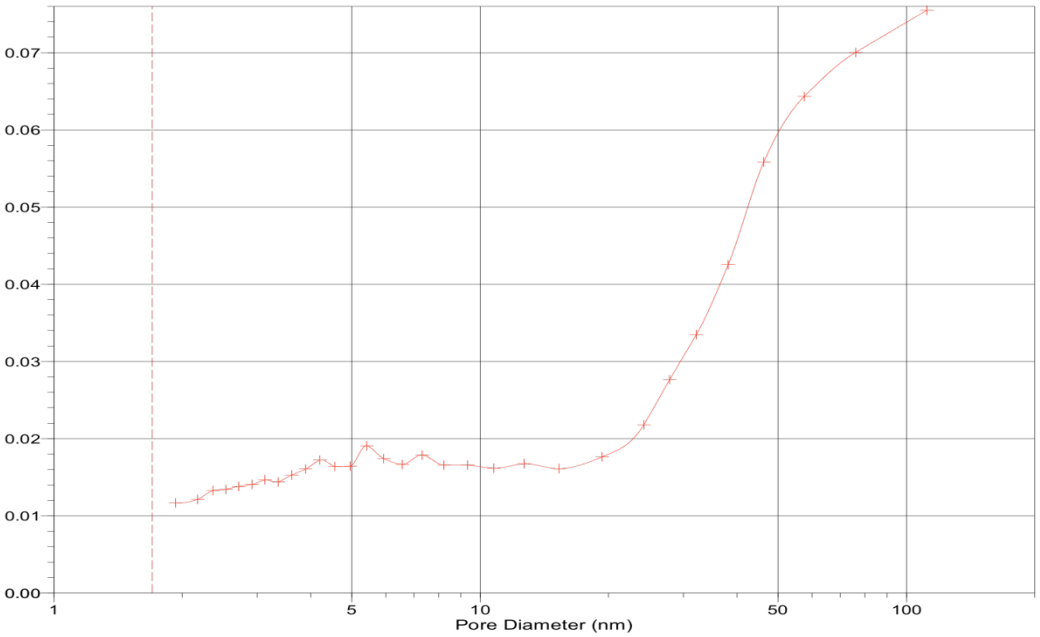


Figure S5. Characterization of the mixed matrix MDP-G1 membrane by N_2 adsorption permporometry. The pore diameters were estimated using the Barrett-Joyner-Halenda (BJH) methodology (4).

A. Barrett-Joyner-Halenda adsorption pore volume



B. Barrett-Joyner-Halenda desorption pore volume

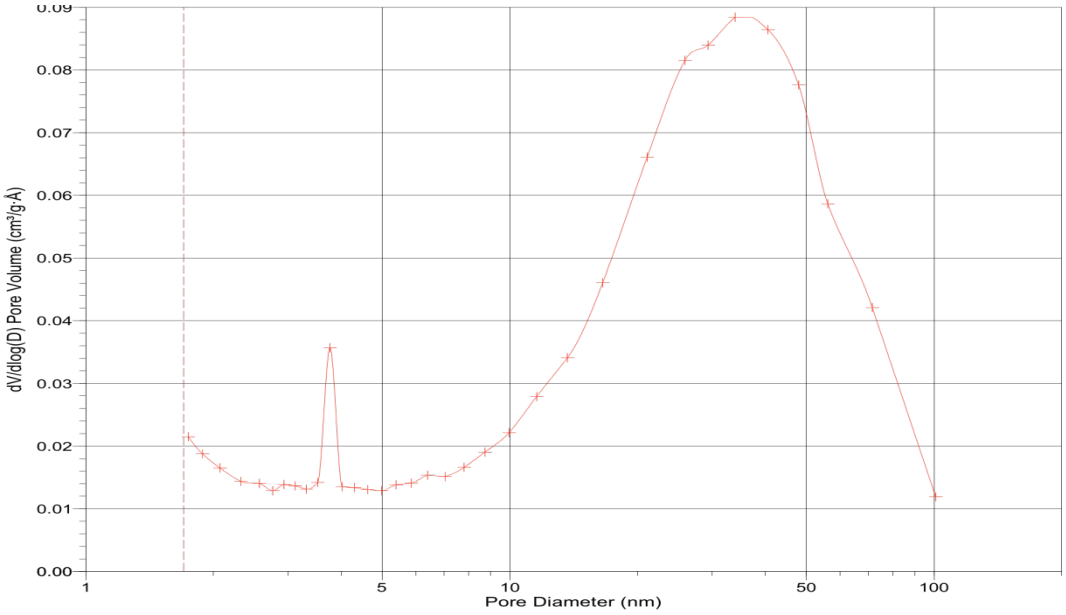


Figure S6. Characterization of the control PVDF membrane by N_2 adsorption permporometry. The pore diameters were estimated using the Barrett-Joyner-Halenda (BJH) methodology (4).

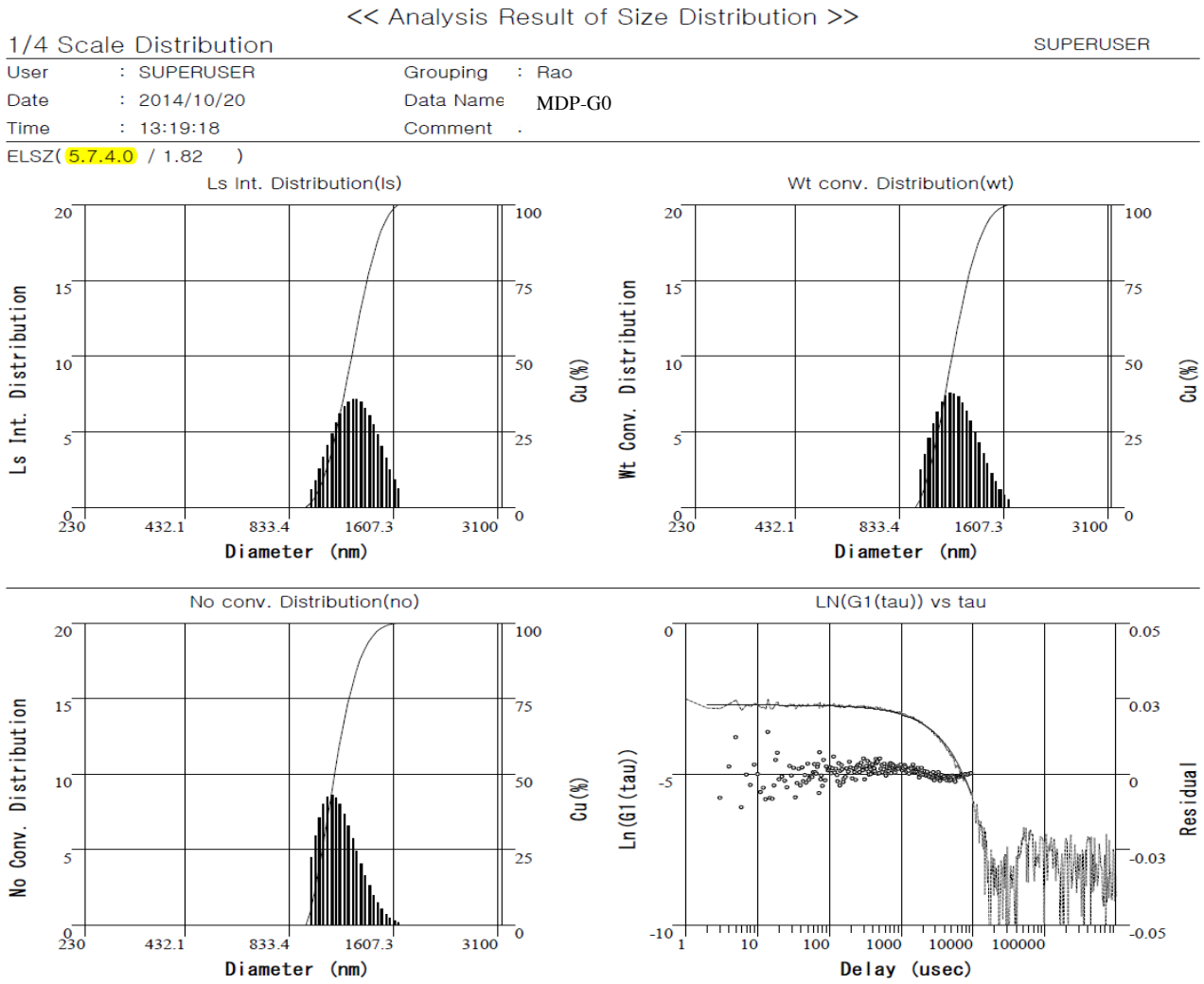


Figure S7. DLS measurements of particle size distribution for the mixed matrix MDP-G0 membrane with *in situ* synthesized crosslinked PAMAM particles. The membrane was dissolved in TEP.

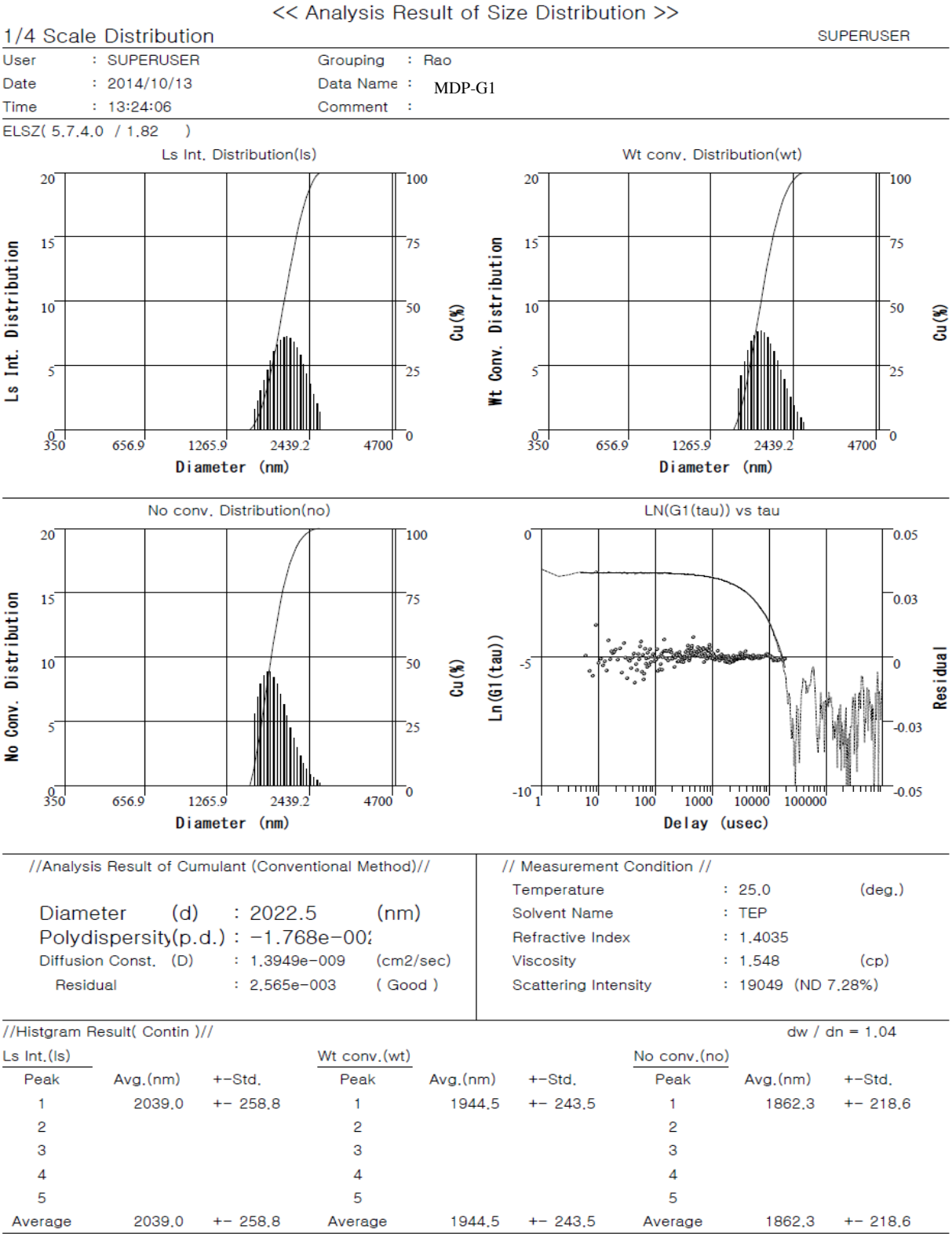
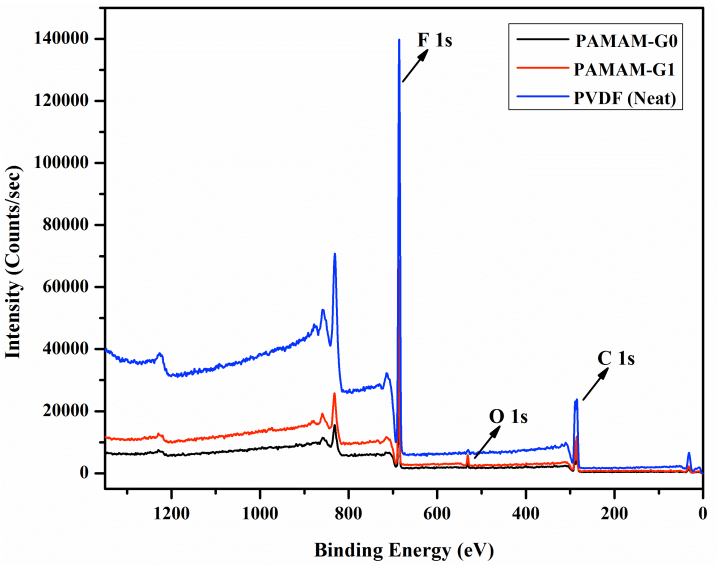


Figure S8. DLS measurements of particle size distribution for the mixed matrix MDP-G1 membrane with *in situ* synthesized PAMAM particles. The membrane was dissolved in TEP.

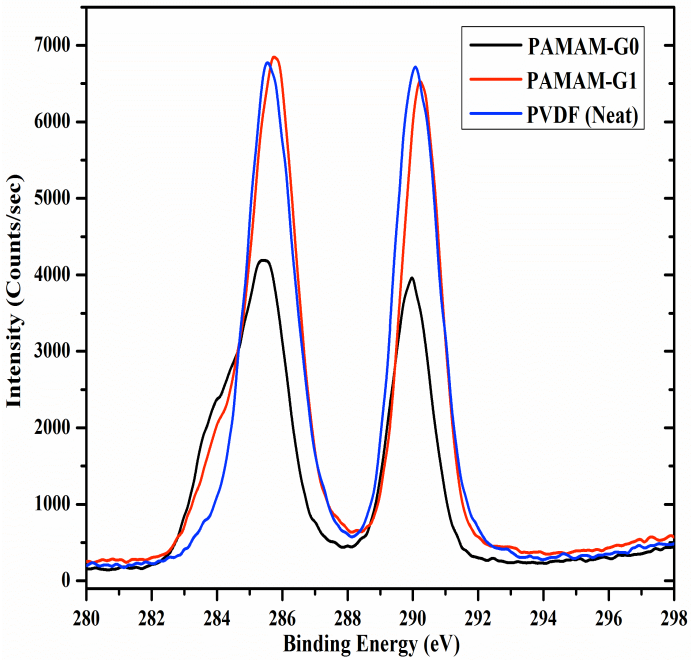
A. Overall scans



B. Surface compositions

Membrane	Atomic concentration (%) by XPS			
	C	F	O	N
PAMAM-G0	58.15	38.92	2.71	0.22
PAMAM-G1	52.62	43.1	3.81	0.47
PVDF (Neat)	51.71	48.29	---	---

C. C1s scans



D. O1s scans

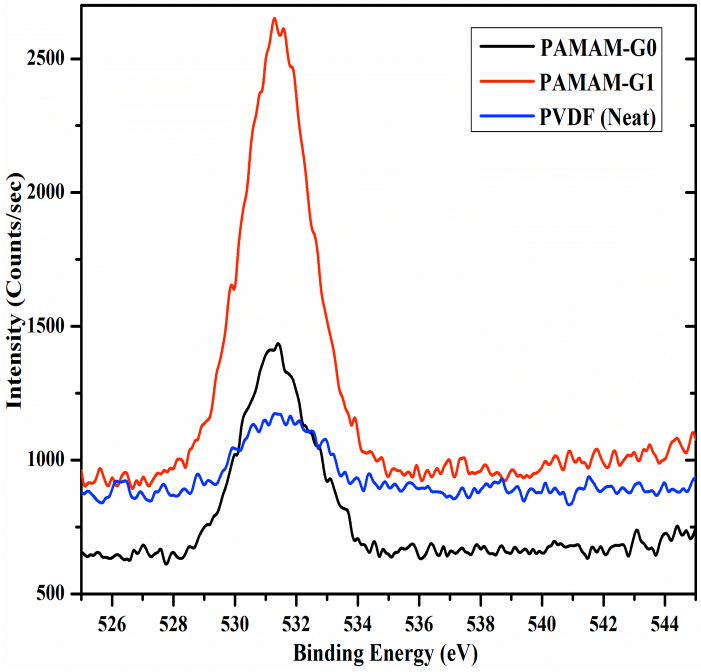
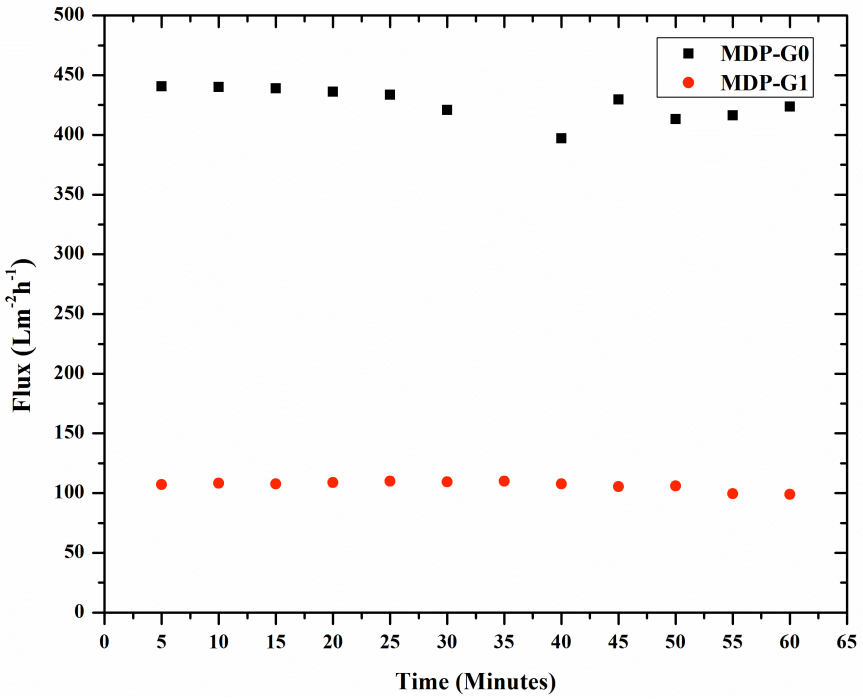


Figure S9. XPS spectra of the control PVDF membrane and mixed matrix PVDF membranes with *in situ* synthesized PAMAM particles. The estimated composition of each membrane is listed in Table S2.



Time (Minutes)	DIW Flux @ pH 7.0 (LMH)	
	MDP-G0	**MDP-G1**
0	0	0
5	440.66	107.14
10	440.11	108.24
15	439.01	107.69
20	436.26	108.79
25	433.52	109.89
30	420.88	109.34
35	433.52	109.89
40	397.25	107.69
45	429.67	105.49
50	413.19	106.04
55	416.48	99.45
60	423.63	98.9
Average	**427.02**	**106.55**
SD	**13.20**	**3.71**

Figure S10. DIW flux of the mixed matrix MDP-G0 and MDP-G1 membranes as a function of filtration time at 2 bar. The estimated composition of each membrane is listed in Table S2.

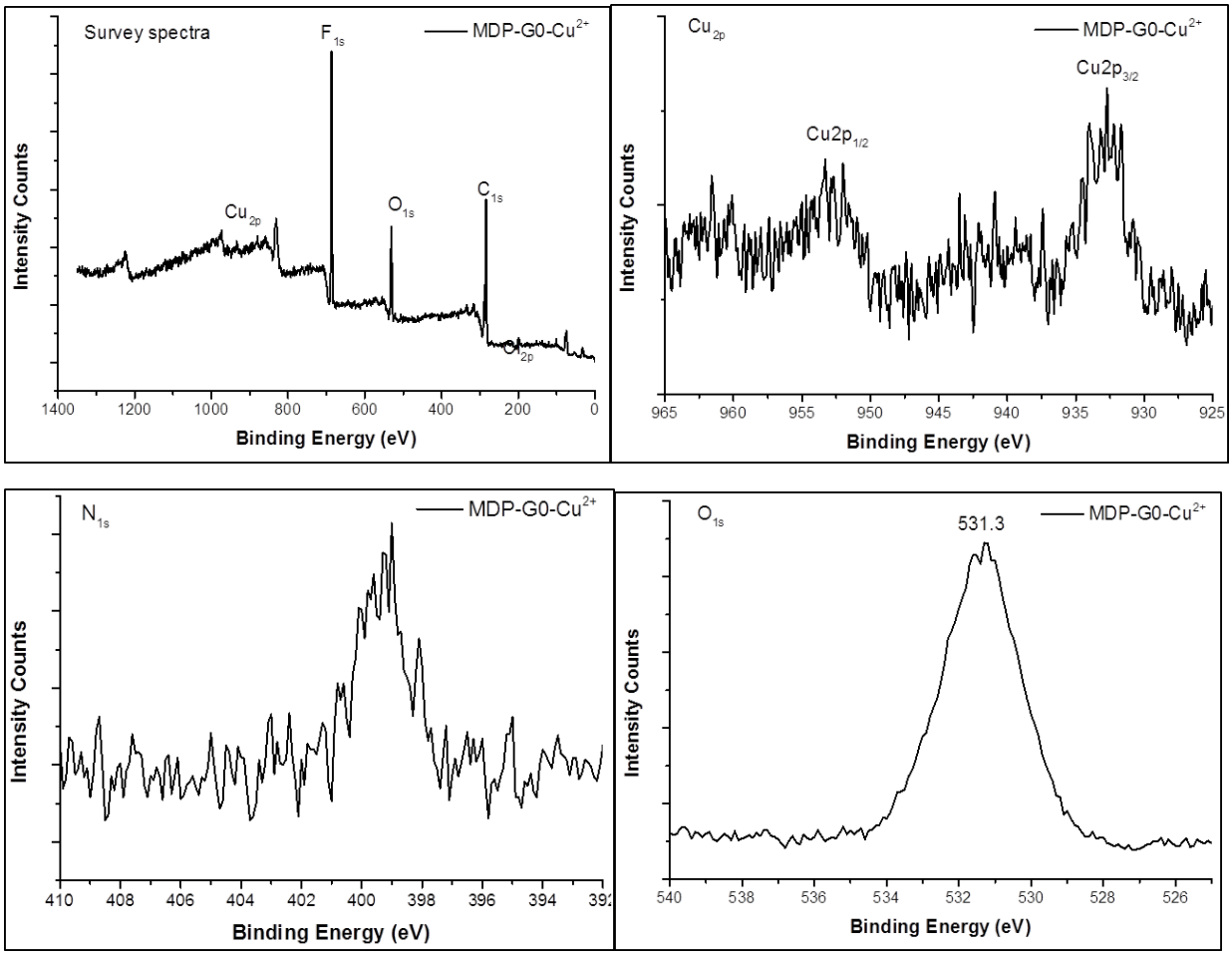
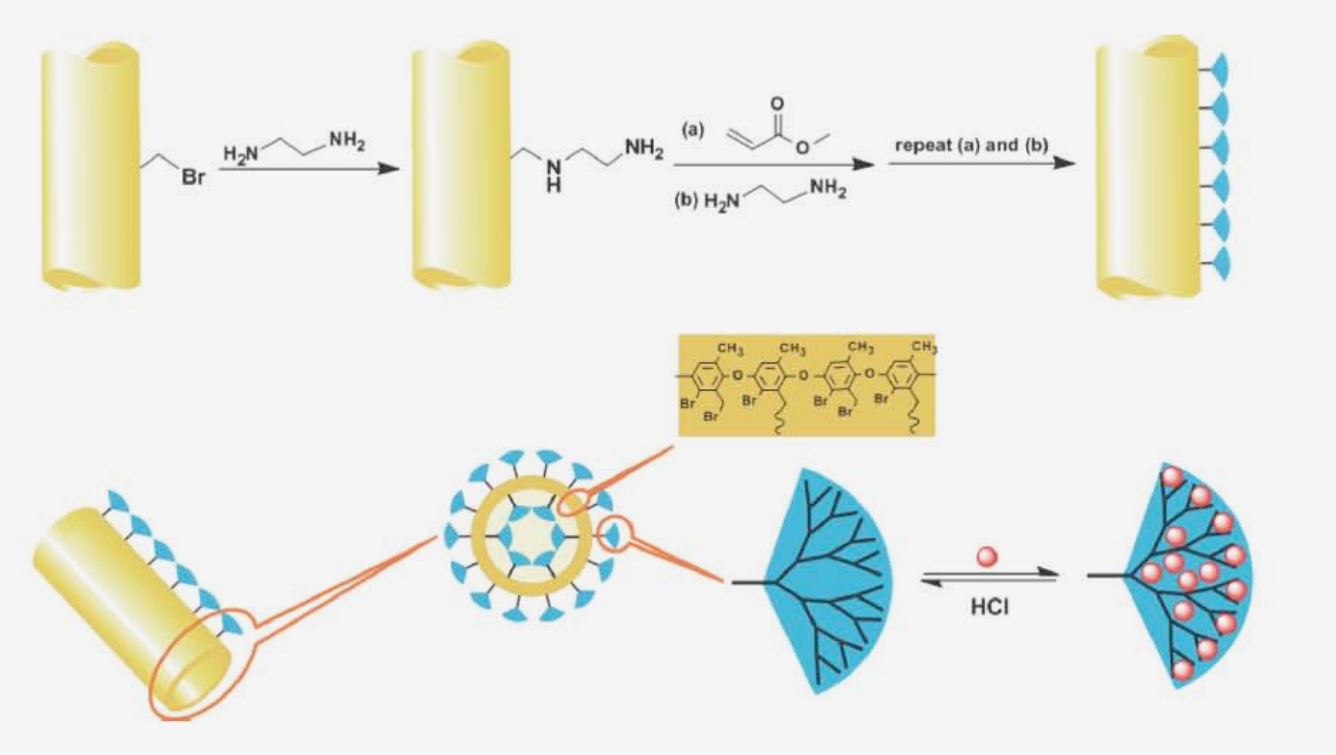


Figure S11. XPS spectra of the Cu(II) loaded mixed matrix PVDF MDP-G0-Cu^{2+} membrane with *in situ* synthesized PAMAM particles. The estimated composition of each membrane is listed in Table S2.

A. Membrane preparation



B. SEM images of a Cu(II) loaded G3-NH_2 Dendronized PAMAM hollow fiber membrane

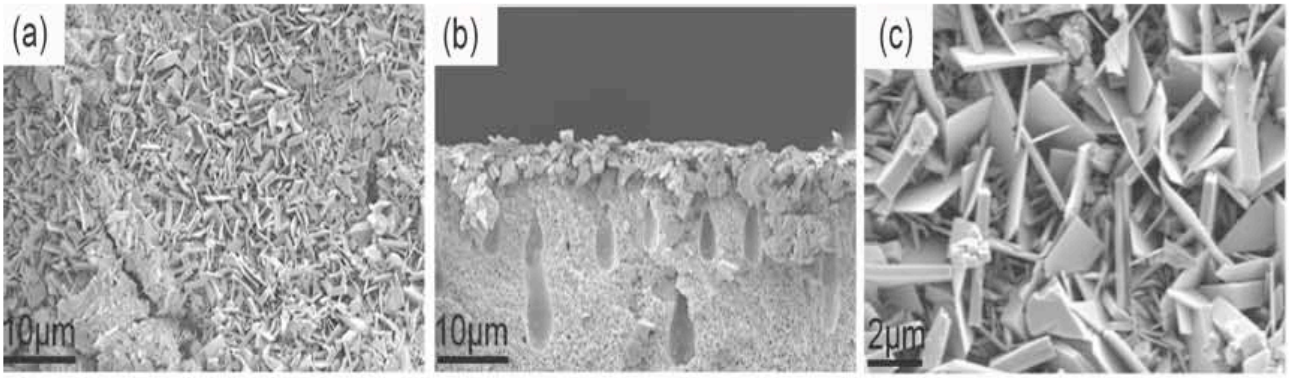


Figure S12. Dendronized PAMAM bromoethylated poly(2,6-dimethyl-1,4-phenylene oxide (BPPO) hollow fiber membranes (HFMs) [7]. A. Membrane preparation and B. SEM images of a G3HFM following immersion of a 50-mg sample in an aqueous solution (8 mL) of $Cu_2(OH)_3Cl$ with a Cu(II) concentration of ~12 mg/L at room temperature for 72 h. The SEM images show the precipitation of $Cu_2(OH)_3Cl$ crystals on the surface of the G3-NH_2 dendronized PAMAM HFM. The SEM images of the Cu(II) laden PAMAM HFM were acquired following sample free-drying using field emission scanning electron microscopy (FESEM, SIRION 200 Series, FEI Corporation) at an acceleration voltage of 5 Kv.